



## Silicon Electrolyte Interface Stabilization (SEISta)

Anthony Burrell

National Renewable Energy Laboratory

Project ID # **bat436**



This presentation does not contain any proprietary, confidential, or otherwise restricted information.

## Timeline

- October 1<sup>st</sup> 2016 - September 30<sup>st</sup> 2019.
- Percent complete: 80%

## Budget

- Funding for FY20: \$3800K

## Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

## Partners

- Six Laboratory Team lead by NREL:
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
  - Pacific Northwest National Laboratory
- UC Berkeley, Colorado University Boulder, Colorado School of Mines, University of Rhode Island



Si anodes are ~10x higher capacity than graphite anodes

1. Si anodes have three major challenges to commercialization

- High Capacity Fade
- Poor Shelf Life
- Electrode formulation/stability

2. SEI formation in Si much more complex than in graphite, and seems to be dependent on initial state and history

- Large volume expansion on alloying
- Extensive gas formation

### **Objective:**

Improve calendar life and understand initial stages of SEI formation by understanding intrinsic chemical reactivity of Si electrodes

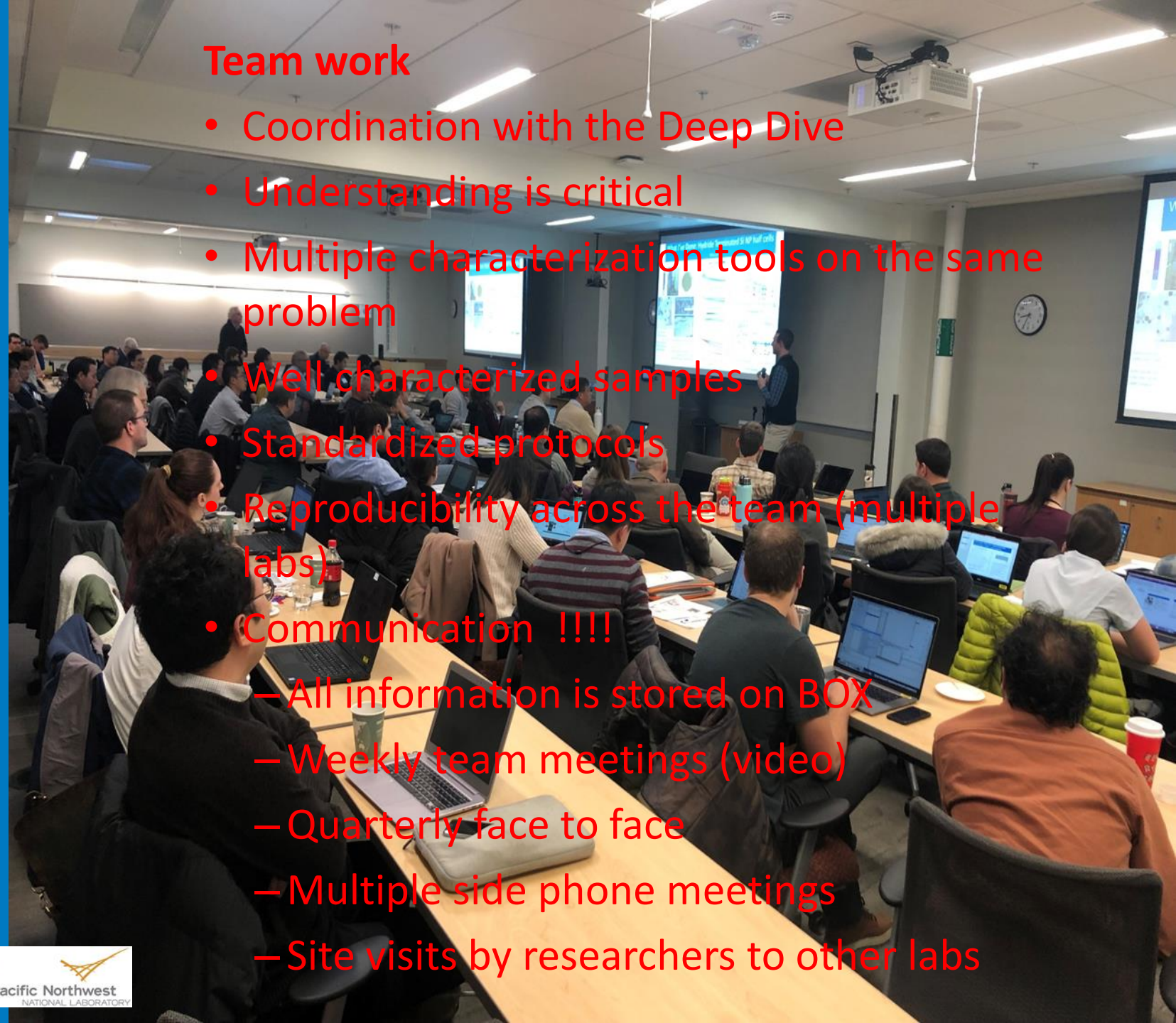
# Approach

## Critical Questions:

- What are the properties of the lithiated silicon electrolyte interface?
- What is the Silicon SEI made of and what reactions are contributing to it?
- How fast does the Silicon SEI grow?
- Does it stop growing?
- Is it soluble?
- Can it be stabilized?

## Team work

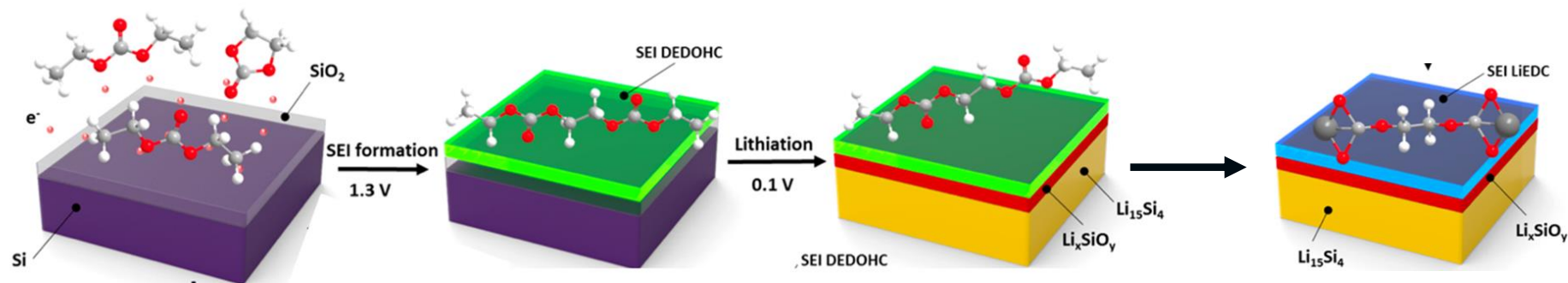
- Coordination with the Deep Dive
- Understanding is critical
- Multiple characterization tools on the same problem
- Well characterized samples
- Standardized protocols
- Reproducibility across the team (multiple labs)
- Communication !!!!
  - All information is stored on BOX
  - Weekly team meetings (video)
  - Quarterly face to face
  - Multiple side phone meetings
  - Site visits by researchers to other labs



# FY20 Milestones

1. Have demonstrated ability to make model electrodes of Mg-Si zintl compounds and compared SEI chemistry to silicon using XPS, STEM-EDS and FTIR/Raman. **Q1 Complete**
2. Have established experiments and protocols for understanding the factors that affect safety in silicon anodes, with a specific focus on highly exothermic reactions that occur at silicon electrodes. **Q1 Complete**
3. Have determined the affect that CO<sub>2</sub> has on the stability of SEI formation on model electrodes, but examining the changes in the nature of the SEI (XPS, and FTIR/Raman and quantitate electrochemical measurement) as a function of CO<sub>2</sub> concentration. **Q2 Complete**
4. Have determined zintl phase formation mechanism and its effect on SEI with model systems including Si NPs, Si wafer, a-Si thin film using XPS, AFM/SSRM, STEM-EDS and FTIR/Raman. **Q2 Complete**
5. **Go/NoGo** on production of tin-silicon alloys to be determined by the ability of the alloys to be prepared in 1g quantities and a demonstration that the alloys exhibit greater cyclic life than the pure metals alone. **Q2 Complete**
6. Have determined the chemistry and interfacial properties (e.g. nature of the chemical bonding at the surface of Si and the organic material) of LiPAA/Si interfaces as a function of charge (OCV, 0.8V, 0.4V, 0.15V, 0.05V) and drying temperature (100, 125, 150, 175, 200C). **Q3**
7. Have determined how binder changes the stress/strain on silicon electrodes as a function of state of charge by varying Si NP size and surface functionally utilizing both 2 or three dimensional model systems. **Q3**
8. Have implemented protocols that enable comparisons of safety responses in silicon anodes as a metric for improving safety in silicon cells. **Q3**
9. Have published a document that will enable other research and development groups to analyze stability of the SEI on a silicon-based anode, thus enabling developers or researchers to continually improve silicon cell stability (joint milestone with the Silicon Deep Dive). **Q4**
10. Have understood how the nature and amount of formed/soluble SEI species varies with electrolyte, binder, and Si anode (with surface functionalization) using GC-MS, (in-situ) FTIR/Raman and XPS. **Q4**

# SEISta – Approach and Overview



[J. Phys. Chem. C 2017, 121, 14476–14483](#)

**Overarching Mission:** Develop a stable SEI layer for Silicon Anodes to enable the use of intermetallic anodes for lithium ion batteries.

This is not a new challenge but we believe that the difficulties working with silicon have precluded a “quick fix” to long term stability of silicon electrodes.

**We require a more foundational understanding of the formation and evolution of the SEI on silicon.**

**Understand first, fix later!**

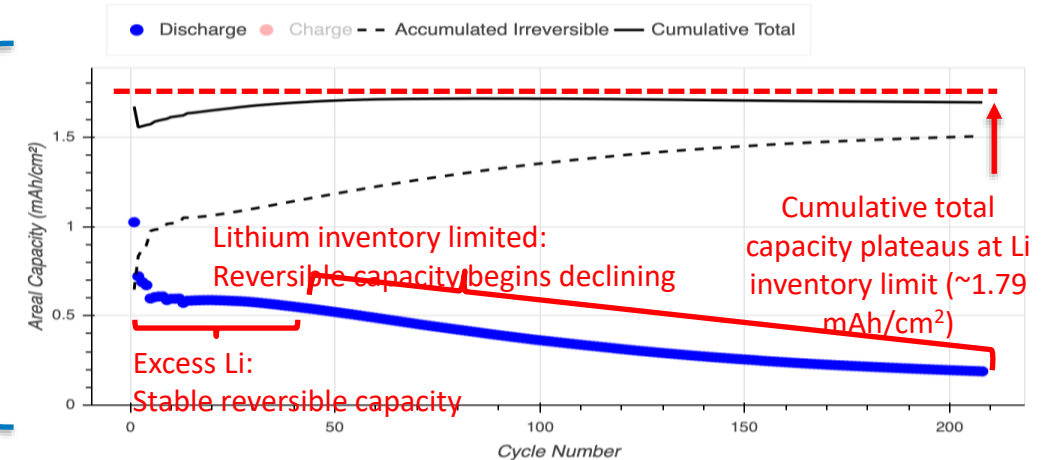
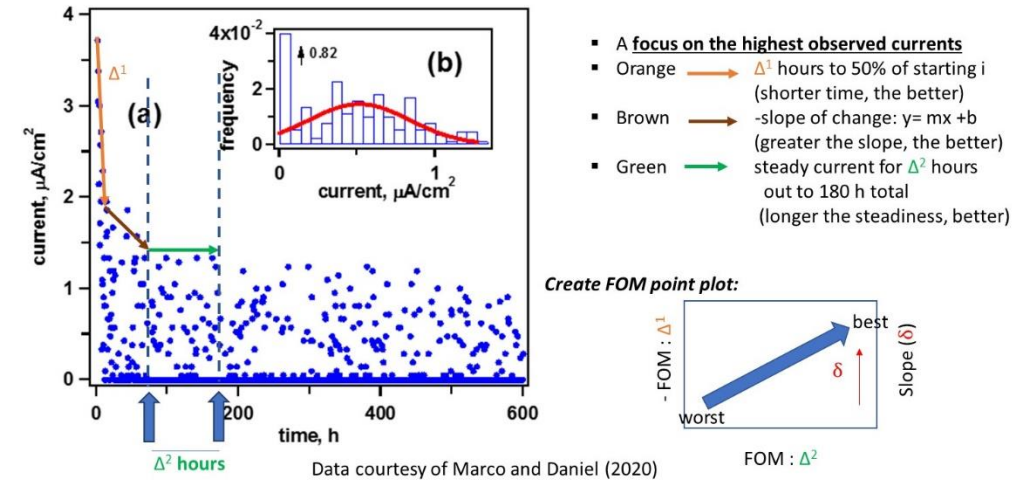
# Standardized Testing Protocols for Predicting Full-Cell Lifetimes

## Key Concepts:

- Full-cell calendar and cycle lifetimes can be predicted using data from short standardized testing protocols.
- Voltage hold tests use figure-of-merit approach to project calendar lifetimes by measuring lithium consumption rates.
- Cycling tests measure accumulated irreversible capacity (AIC) to predict lifetimes:

$$\sum_{\text{cycle } n=1}^n Q_{\text{lithiation cycle } n} - Q_{\text{delithiation cycle } n} = AIC$$

- AIC corresponds to consumption of lithium inventory and capacity fade in full-cells.
- Lifetimes of full-cells can be predicted using AIC values determined from short half-cell experiments.

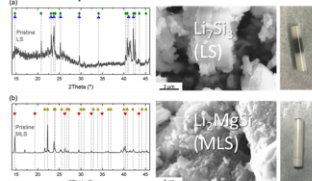


Standardized testing for cyclic life and calendar life is part of a stage gate process for developments.

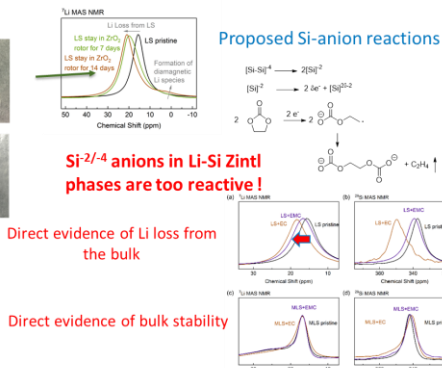
# Understanding the Li-Mg-Si TERNARY ZINTL SYSTEM - Approaches

FY19

• Comparison of reactivities



Instability of lithium silicides (identified last year) bulk and surface can be largely mitigated by incorporation of  $M^{2/+3}$  which provide coulombic stabilization in the Zintl phase. See BAT388 for applications in half and full cells



Direct evidence of Li loss from the bulk

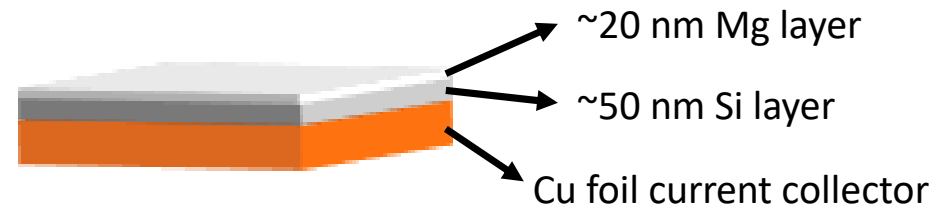
Direct evidence of bulk stability

Binghong Han, Chen Liao, Fulya Dogan, Stephen E. Trask, Saul H. Lapidus, John T. Vaughan, Baris Key, *Energy & Environmental Science*, 2019, submitted

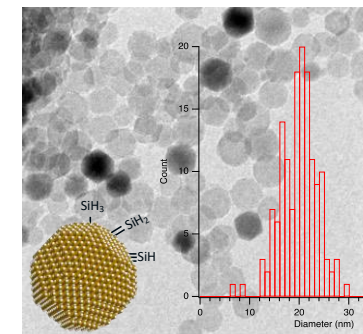
Using understanding gained in previous work suggests that stabilizing the lithium silicide may be a route to longer life silicon anodes.

## 1) Preparation of well controlled model samples

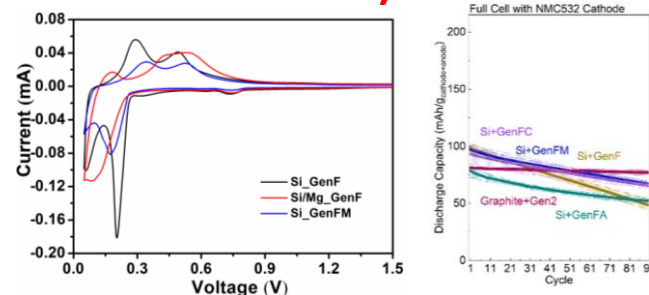
Thin film samples



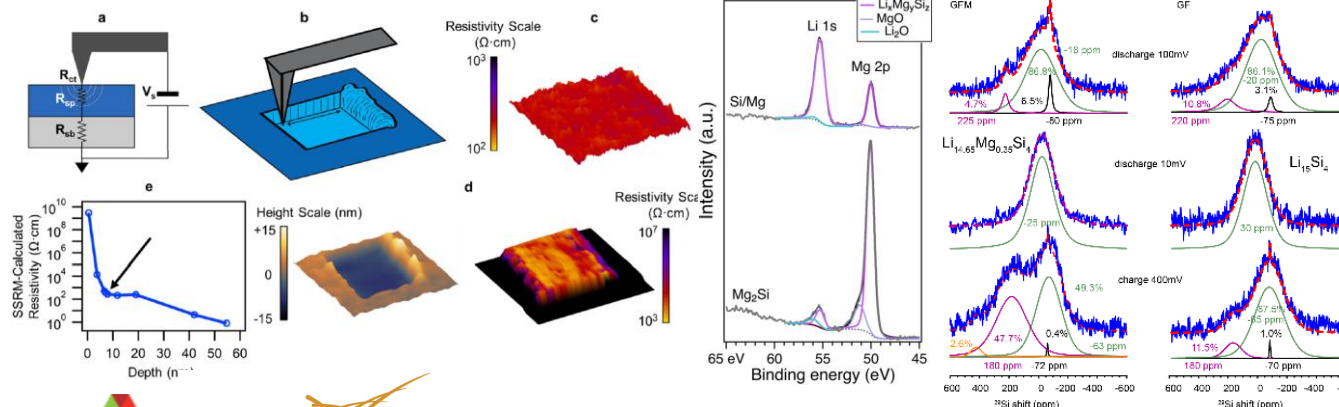
Well defined nanoparticles samples



## 2) Detailed electrochemical analysis

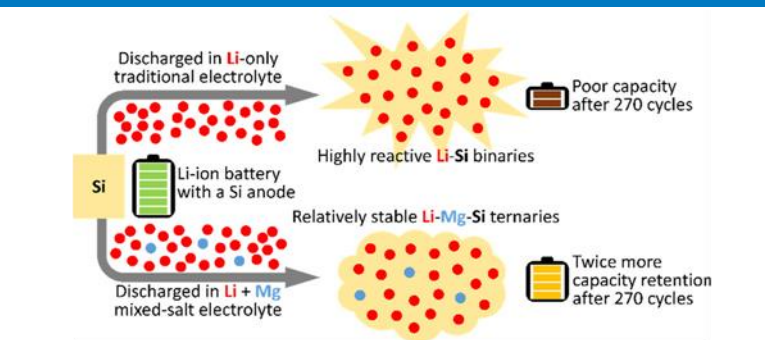


## 3) A lot of characterization

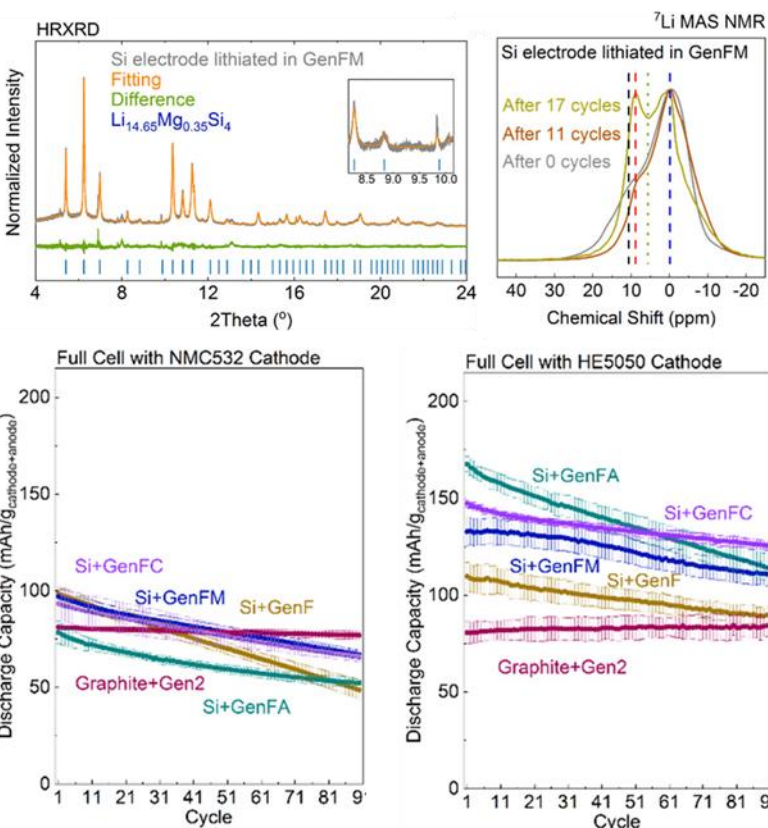


Understanding the how the zintl phase system affects SEI formation and evolution is a key milestone for FY20

# Mechanistic Understanding of Zintl Phase in the SEI



Co-insertion of Mg and Li cations into the Si electrode during the lithiation process, forming less reactive metal-substituted lithium silicide species in an *in situ* fashion and reducing the reactivity of charged Si anodes.



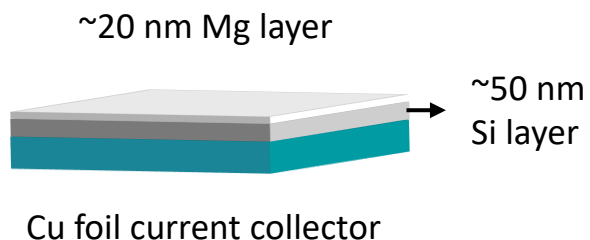
Baris K. et al. ACS Appl. Mater. Interfaces 2019, 11, 29780

Further *ex situ* and *in situ* characterization studies are needed to address...

- What is the formation mechanism of Li-M-Si Zintl phase?
- Where MgO come from and what is the role of MgO in SEI?
- What is the effect of Li-M-Si Zintl phase on SEI?

Mechanistic understanding of Zintl phase in the SEI with model systems (e.g., Si wafer, amorphous Mg-coated Si thin film, and Si nanoparticles)

# Mechanistic Understanding of Zintl Phase in the SEI: Model System II. Amorphous Mg-coated Si Thin Film



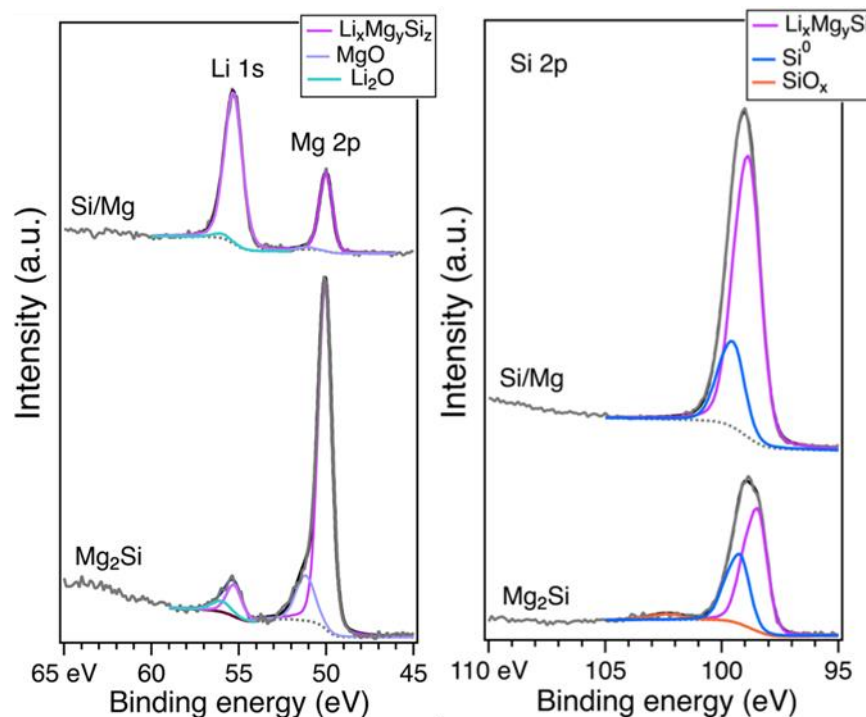
## Electrolytes

GenF: Gen2 + 10 wt% FEC

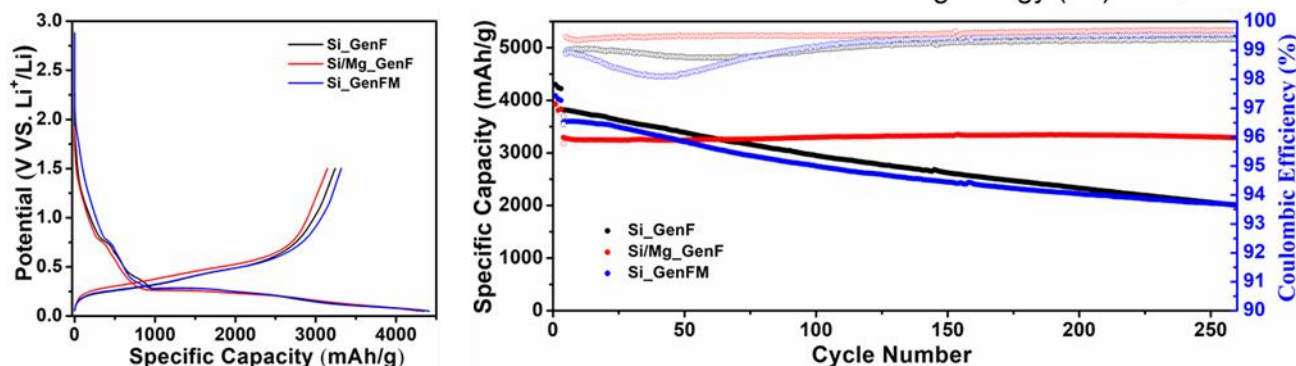
GenFM: GenF + 0.1 M Mg(TFSI)<sub>2</sub>

## Testing protocol:

3 cycles at 0.1C (3.9  $\mu\text{A}/\text{cm}^2$ ), then at 1C in the voltage range of 0.01-1.5 V (vs Li/Li<sup>+</sup>)

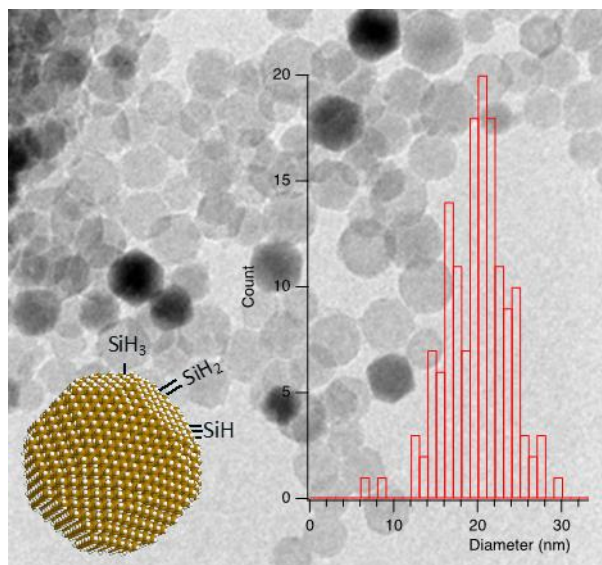


- Amorphous Mg-coated Si electrodes show similar electrochemical behavior compared with those of uncoated Si electrodes.
- Mg coating increases the capacity retention of a Si anode.
- The GenFM electrolyte does not improve the capacity retention for a Si thin film, indicating different underlying chemistry and structure of formed Zintl phase.
- Both the Mg 2p and Si 2p XPS peaks with the presence of Li 1s peak in the lithiated Mg-coated Si thin film electrode suggest the potential formation of ternary Zintl phase.



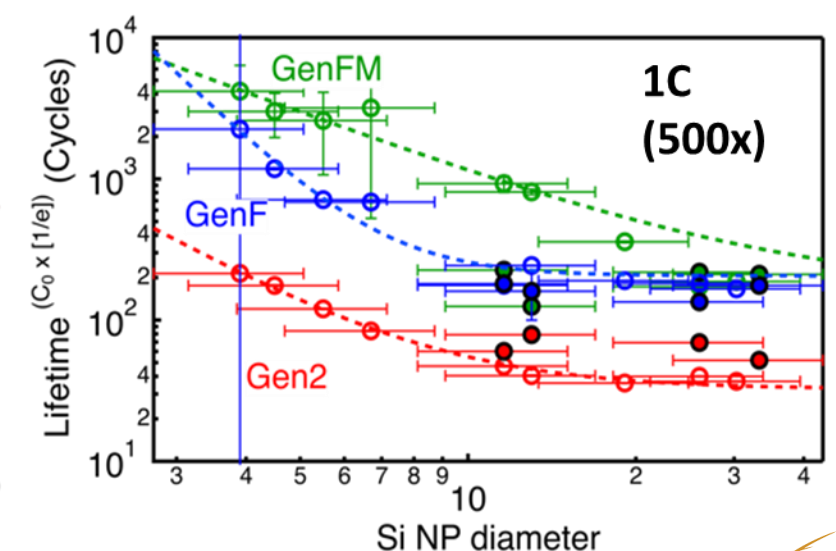
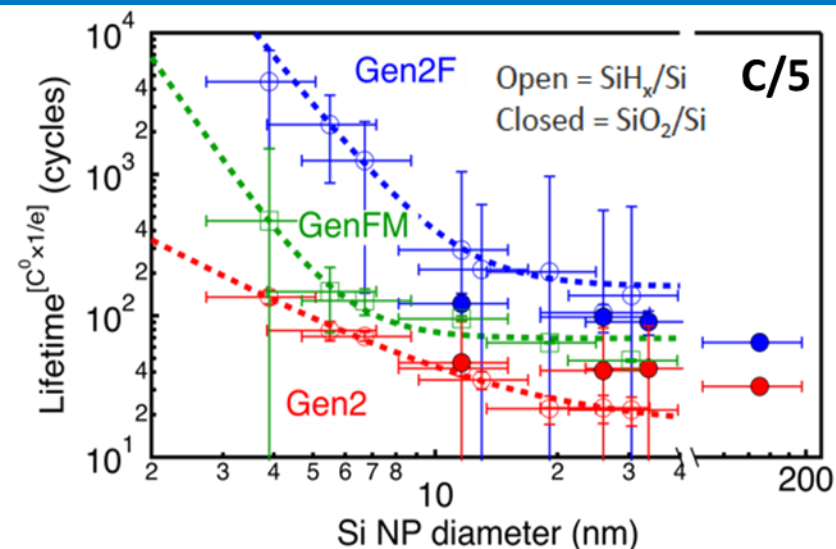
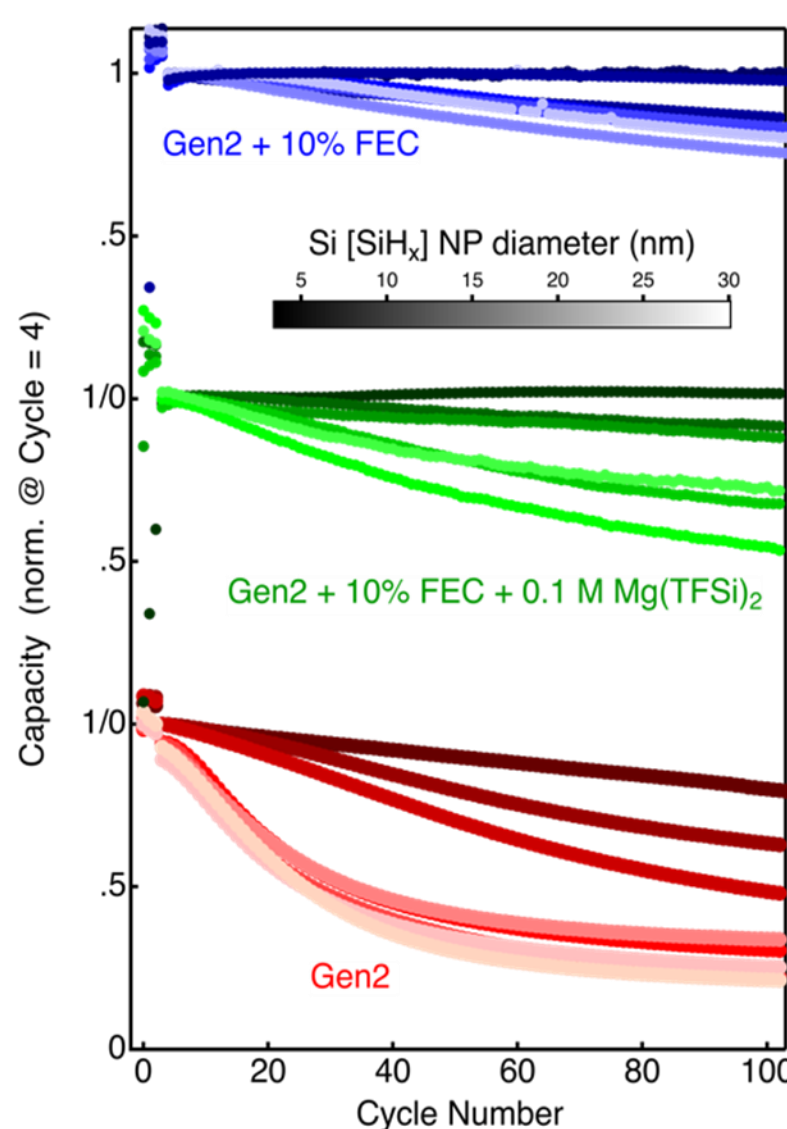
Potentially formed Zintl phase in lithiated amorphous Mg/Si thin films is relatively less reactive and prevents further unwanted reactions, which enables improved electrochemical performance.

# Mechanistic Understanding of Zintl Phase in the SEI: Model System III. Si Nanoparticles



- Electrochemical performance comparison between size, electrolyte, and surface oxide
- Faster cycle rates improves electrochemical performance in a GenFM electrolyte

A variety of factors including surface chemistry, and electrolytes, affects the formation of Zintl phase.

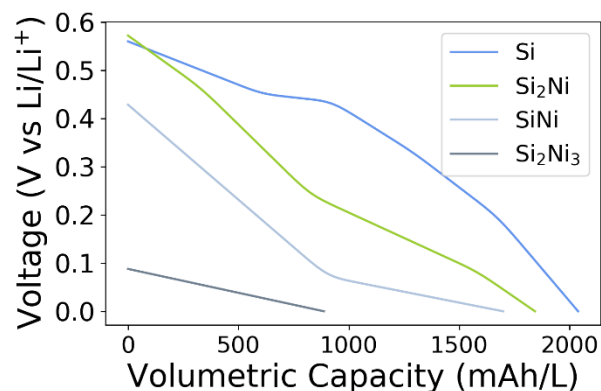


# Tailoring the Si anode through the addition of alloy components



- Si alloys ( $\text{Si}_{1-y}\text{M}_y$ ) have previously been shown to improve cycling performance by:
  - Suppressing Formation of c- $\text{Li}_{15}\text{Si}_4$  phase
  - Lowering cycling voltage
  - Improving Li diffusion
  - Modifying surface reactivity and SEI stability
- Lithiation potential is decreased when alloyed with transition metals such as Ni, Ti, Zr
- Voltage can be tuned by changing Si fraction

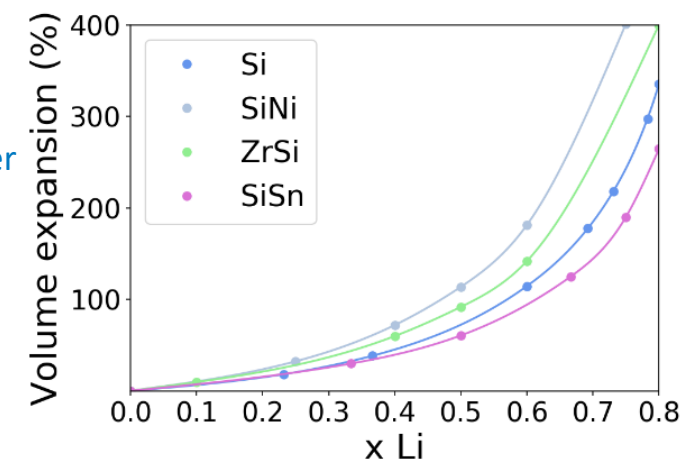
### Lithiation Potentials



**Calculations are being used to help determine the alloys that may have the most positive characteristics for silicon anodes**

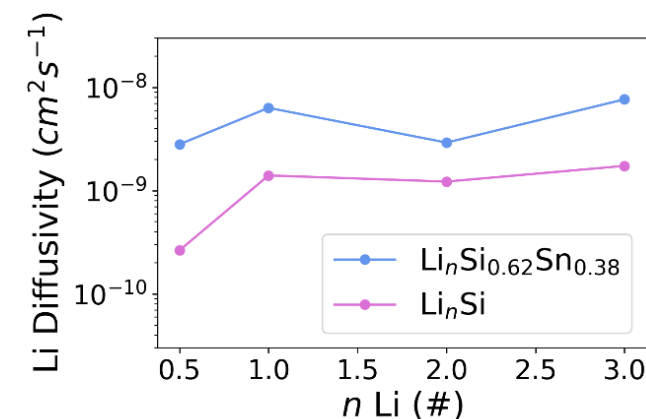
### Volumetric Expansion

- Alloying is not an effective strategy to mitigate volume expansion
  - Favorable Si-M interactions (lower initial volume) tend to increase volumetric expansion
  - Higher initial volumes decrease expansion at the expense of volumetric capacity



### Li Diffusivity

- Li diffusivity can be increased when alloyed with Sn



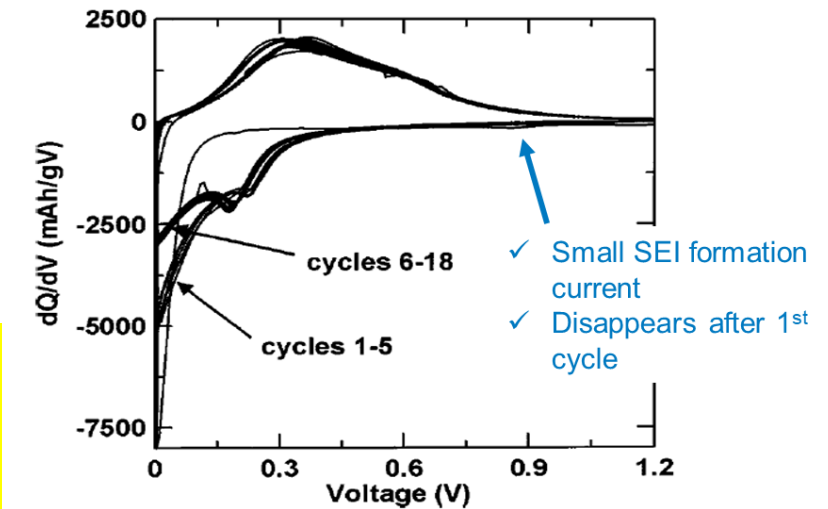
# Go-NoGo on silicon alloys: Favorable Characteristics of Metallic Glasses as Anode Materials = GO

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

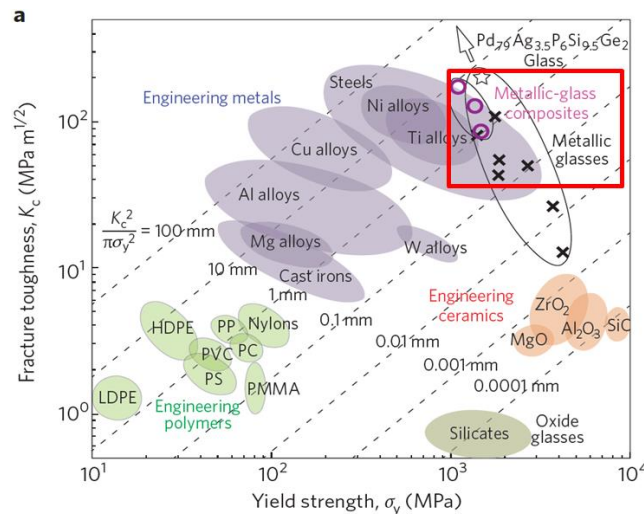
## Reasonable capacity

|                              | $\text{Al}_{1-x-y}\text{Si}_x\text{Ni}_y$<br>( $x = 14 - 25$<br>$y = 8 - 25$ ) | $\text{Al}_{1-x-y}\text{Si}_x\text{Fe}_y$<br>( $x = 12 - 30$<br>$y = 12 - 18$ ) | $\text{Al}_{1-x-y}\text{Si}_x\text{Mn}_y$<br>( $x = 12 - 30$<br>$y = 8 - 25$ ) |
|------------------------------|--|---|--|
| Theoretical Capacity (mAh/g) | 1412 - 2195  | 1678 - 2113   | 1620 - 2120  |

## Better surface stability

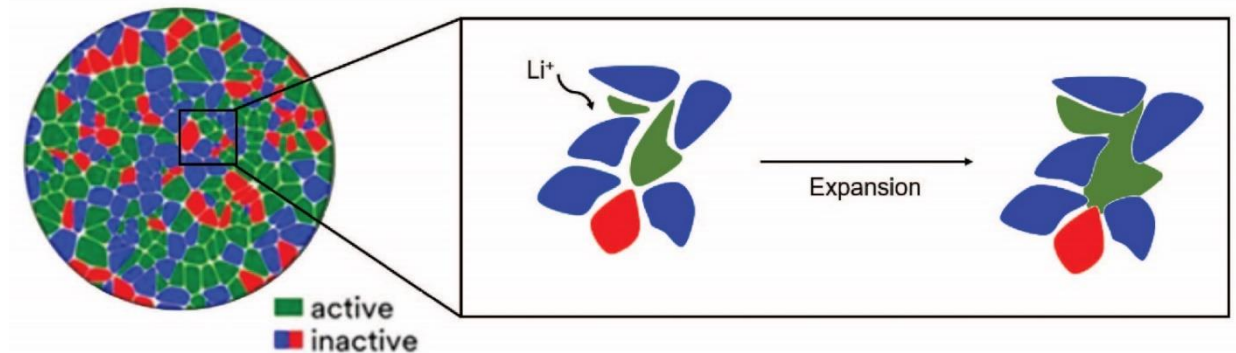


## High fracture toughness



**Silicon Alloys have many positive characteristics that may enable long lived silicon-based anodes.**

## Reduced volume change



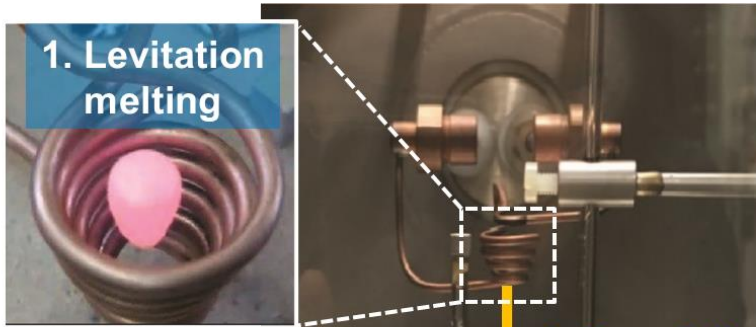
R. Ritchie et al., *Nature Mater*, 2011, 10. P.817-822  
M. D. Fleischauer et al., *J. ECS*, 2004 151(8) A1216-1221

# Bulk Metallic Glass Production & Structure Analyses

## Splat Quenching

Quenches a molten metal droplet by splatting it with two *cold metal surfaces* at cooling rates of  $10^5$ - $10^6$  K/s to produce amorphous alloys

1. Levitation melting



2. Free-fall

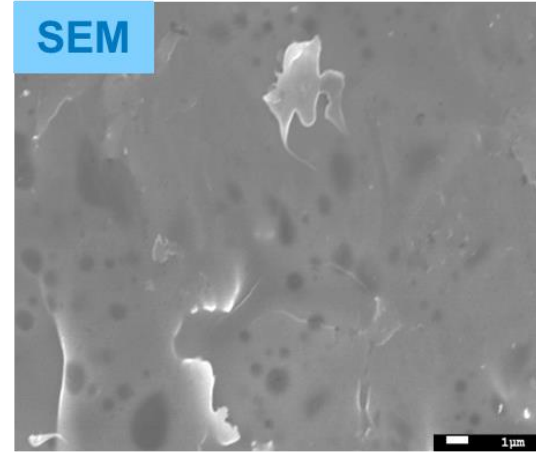


3. Splatting

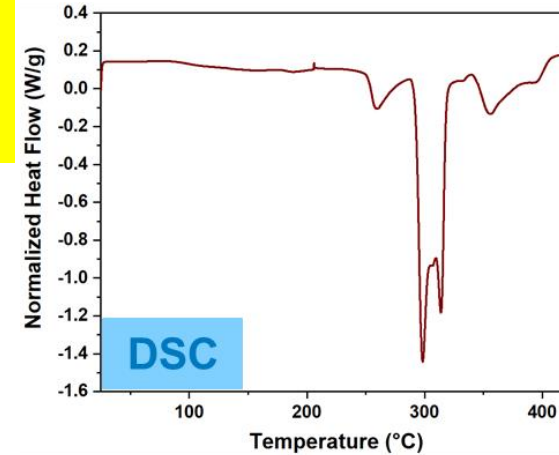
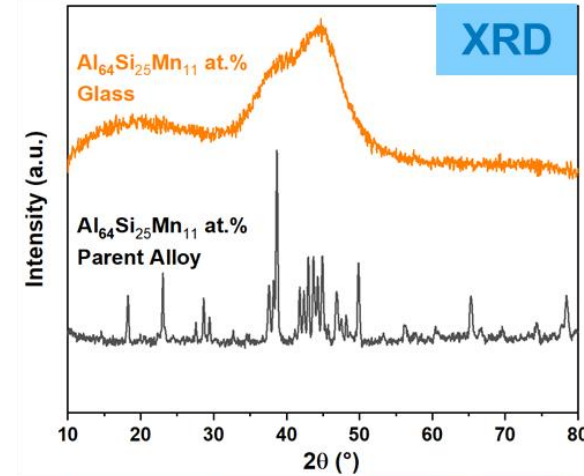


**Bulk synthesis is required to assess the utility of alloys in anodes. Splat quenching has proven an effective method to form the silicon metallic glasses.**

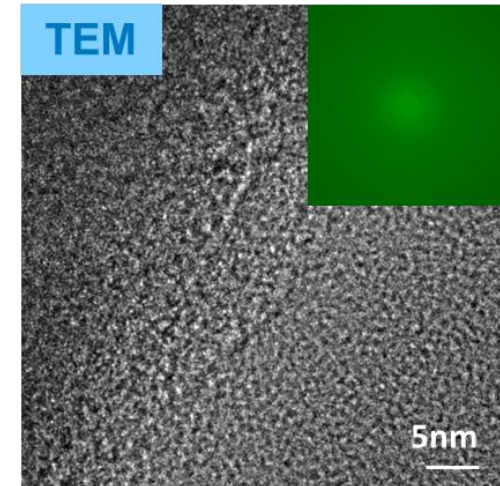
SEM



XRD



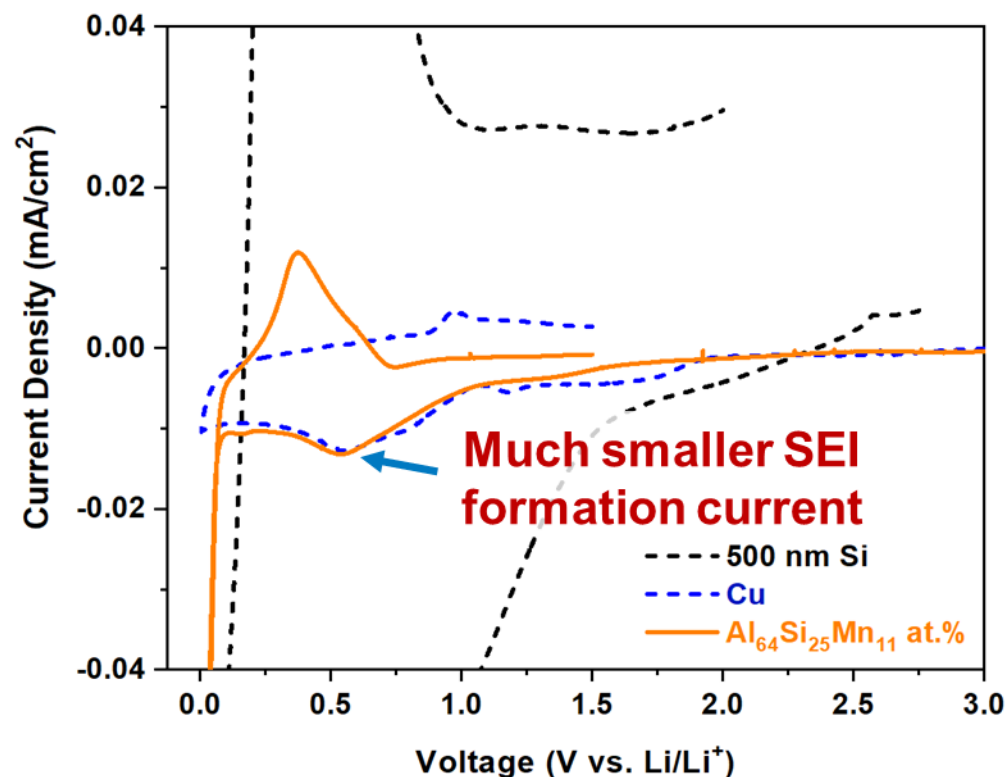
TEM



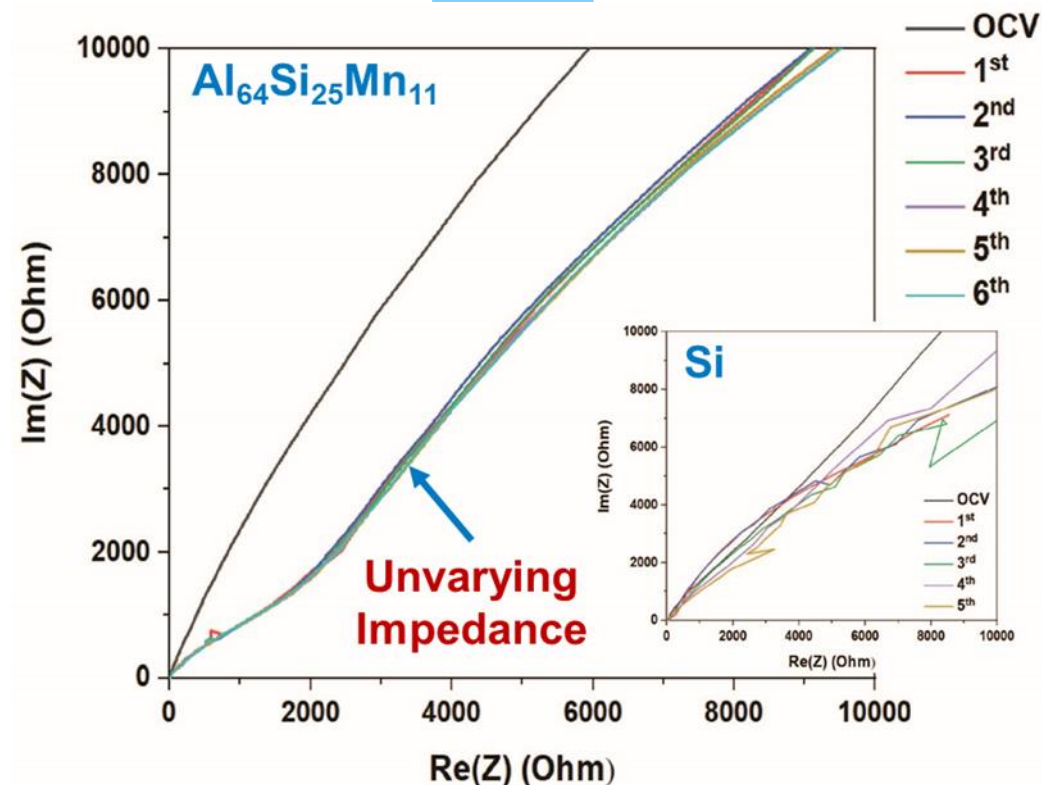
SEM, XRD, DSC and TEM analyses confirms successful fabrication of dense, amorphous metallic glasses

# Interfacial Stability of Metallic Glasses

CV



EIS



**Metallic glasses show much better interfacial stability compared to the pure Si electrode counterpart**

- ✓ Much smaller SEI formation current density
- ✓ Constant cell impedance (Si shows impedance evolution as it cycles)

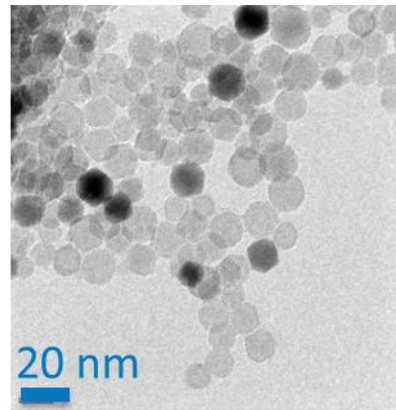
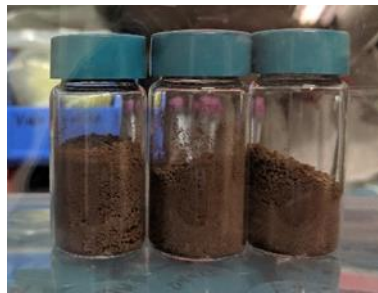
# PECVD Si Nanoparticles Enable Unique Studies on Material Composition

## Key Concepts:

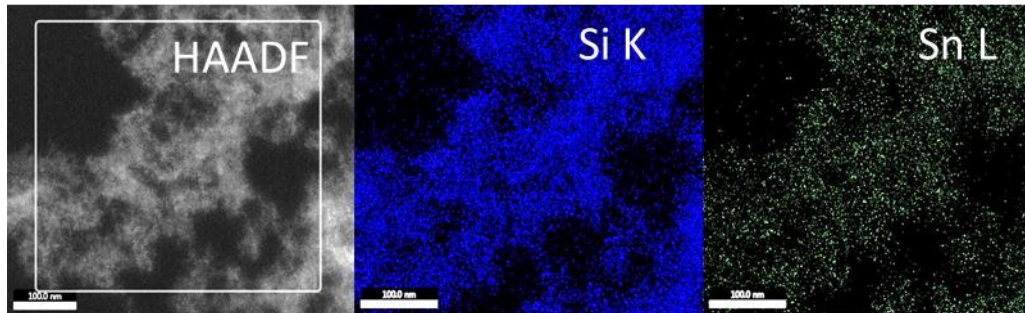
- Nonthermal plasma-enhanced chemical vapor deposition (PECVD) enables synthesis of intrinsic, doped, and alloyed Si NPs (3–50 nm diameter)
- PECVD method capable of grams per day production of hydrogen-terminated, oxide-free Si NPs

### Intrinsic Si NPs

Synthesis of Si NPs  
via PECVD at  
production rates  
of 1.2 g/hr



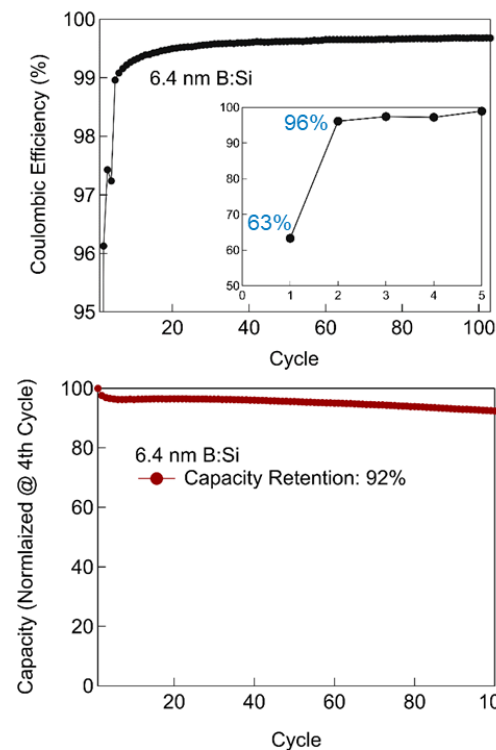
### Si<sub>1-x</sub>Sn<sub>x</sub> Alloy NPs



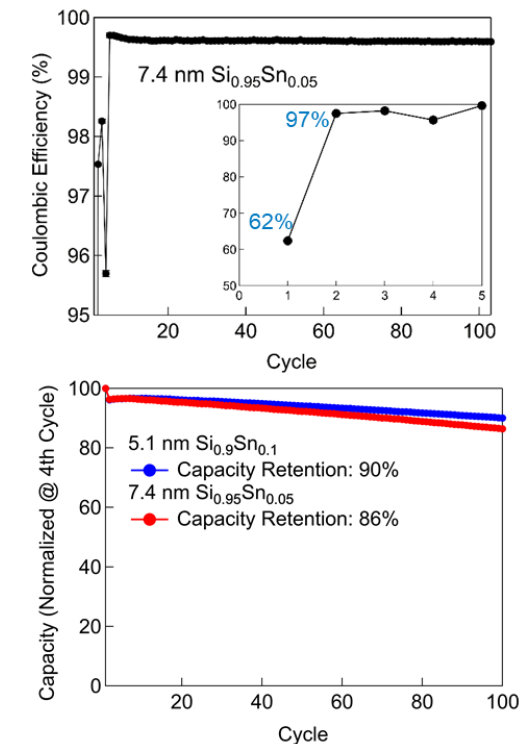
## Key Conclusion:

- Doping and alloying Si NPs accelerates CE stabilization and enhances capacity retention cf. intrinsic Si NPs

### B:Si NPs



### SiSn NPs



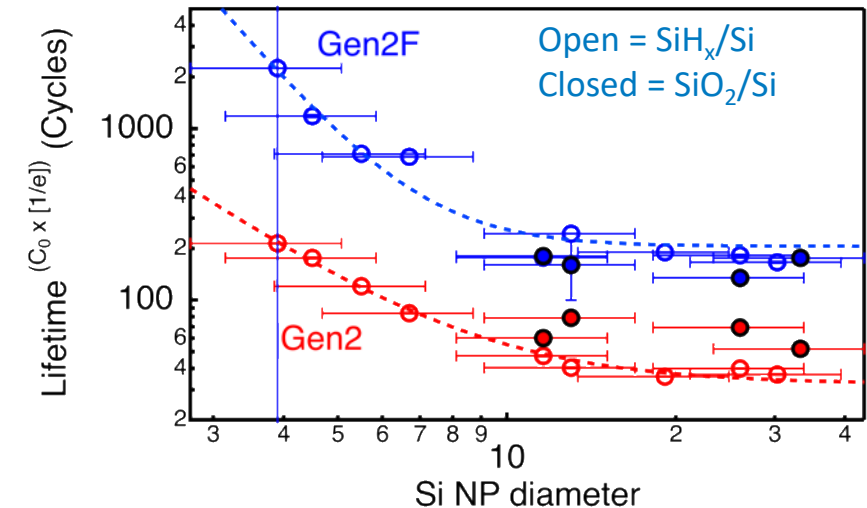
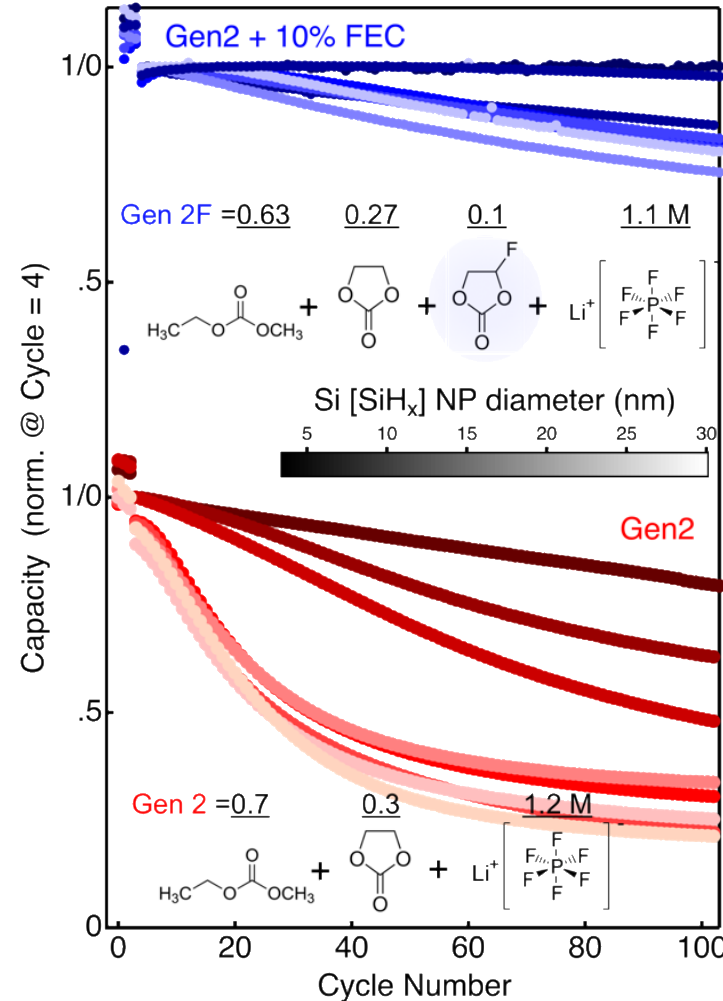
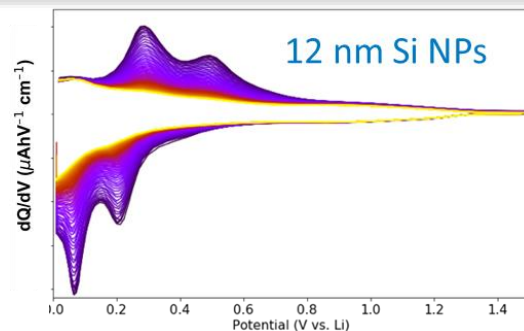
**PECVD enables compositionally controlled nano-particles of alloys for initial evaluation of functional electrode structures.**

# Role of Size, Surface, and Electrolyte in Si Nanoparticle (NP) Electrodes

## Key Conclusions:

- Capacity retention and rate capability increase with decreasing Si NP size (3–30 nm)
- FEC provides stabilization for both  $\text{SiH}_x$  and  $\text{SiO}_x$  surfaces

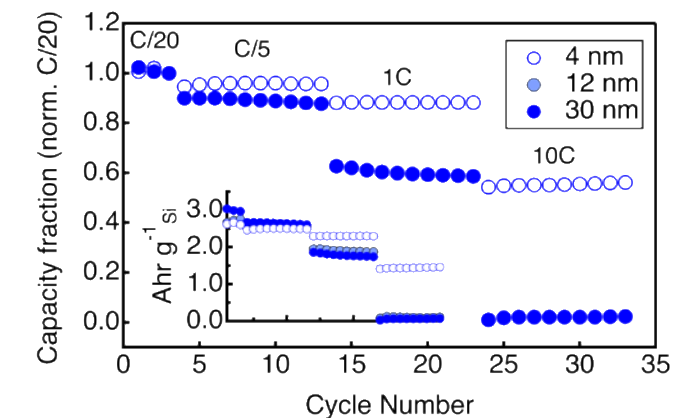
Model Composite Electrodes:  
 15% mass Si NP (3–30 nm)  
 70% mass Carbon ( $\text{C}_{65}$ )  
 15% mass PAA binder  
 Areal capacity:  $\sim 1 \text{ mAh cm}^{-2}$   
 Porosity > 50%  
 Cycled in half-cells (vs Li metal)  
 Cycled 3 @ C/20 then 100 @ C/5



Both Lifetime &  
Rate Capability:



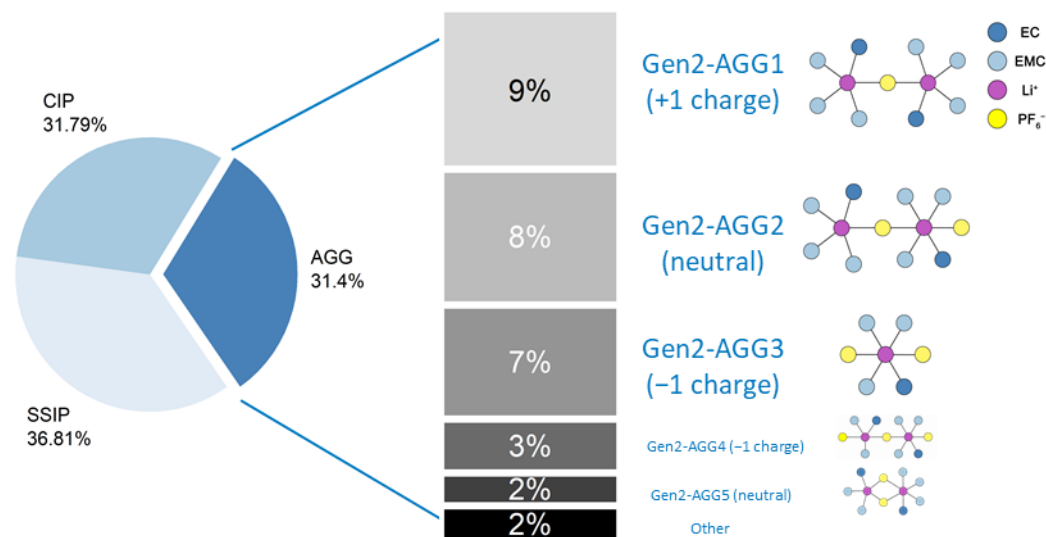
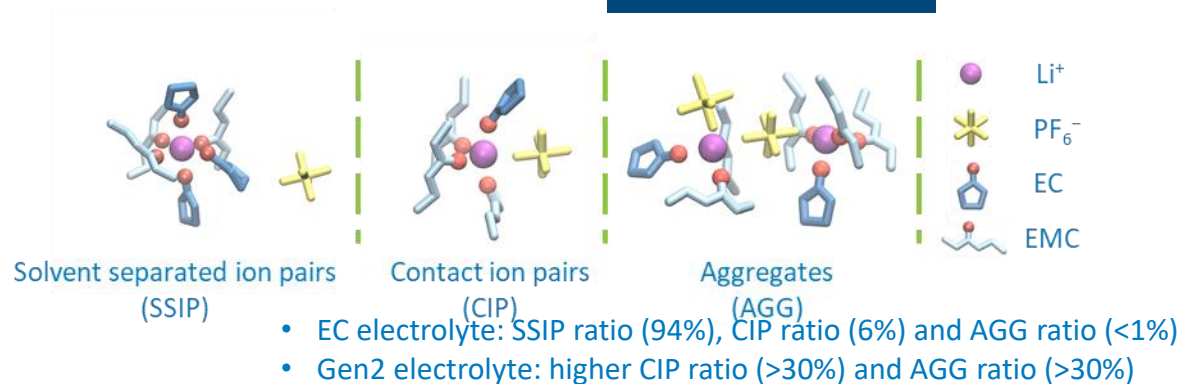
Rate Capability also impacted by Si size



# Solvation structure, reduction behavior and transport properties of Gen2 electrolyte vs EC electrolyte

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

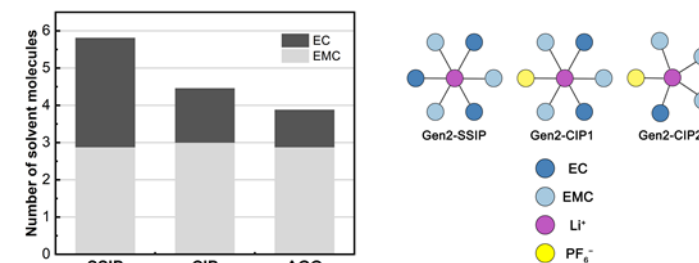
## Solvation structure



**Understanding the nature of the electrolyte and its interaction with the electrode (surface) is critical to determining SEI formation and evolution.**

- At least 19 % within the 31% AGG species are charged species, which contributes to the ionic conductivity

## EMC-Li binding preferred in CIP&AGG



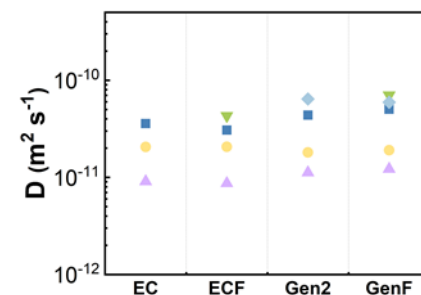
- EC is preferentially pushed out of the solvation shell as  $\text{PF}_6^-$  comes in.
- EMC forms a more stable structure with  $\text{PF}_6^-$ .

## Reduction Behavior

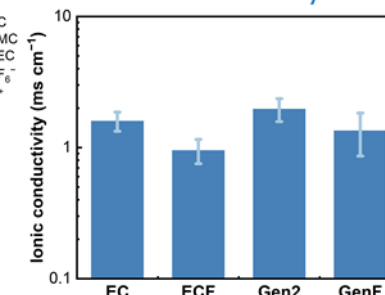
- Reduction potential: EC: c.a. 0.70~0.64 V  
EMC: c.a. 0.45 V
- EC is preferentially reduced and contribute to the initial SEI formation

## Transport properties

### Self-diffusion coefficient



### Conductivity



- Gen2 exhibits higher diffusivity than EC
- Gen2 and EC electrolyte show similar overall conductivity

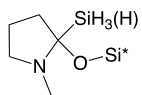
# Electrochemical Behavior with Tailored Si NP Molecular Surface Chemistries

## Key Concept:

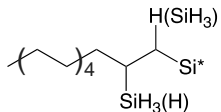
- Rationally designing the Si active material surface chemistry can lead to an electrochemically and chemically stable interface, maximizing capacity retention and minimizing irreversible lithium consumption

## Types of surface chemistry modifications:

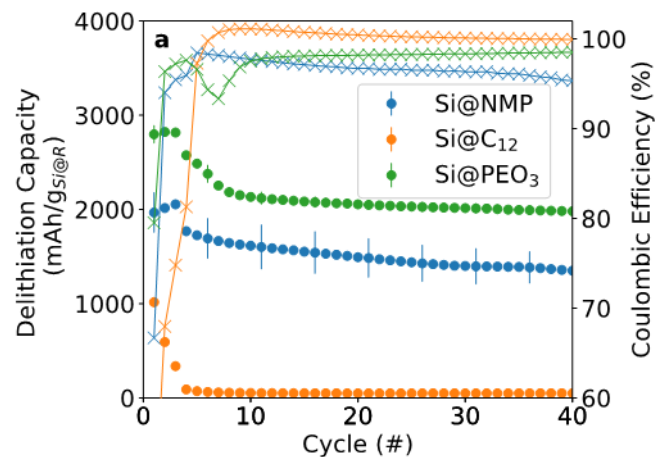
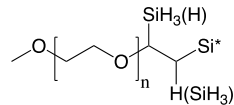
**Control:** Si@NMP



**Non-polar:** Si@C<sub>12</sub>



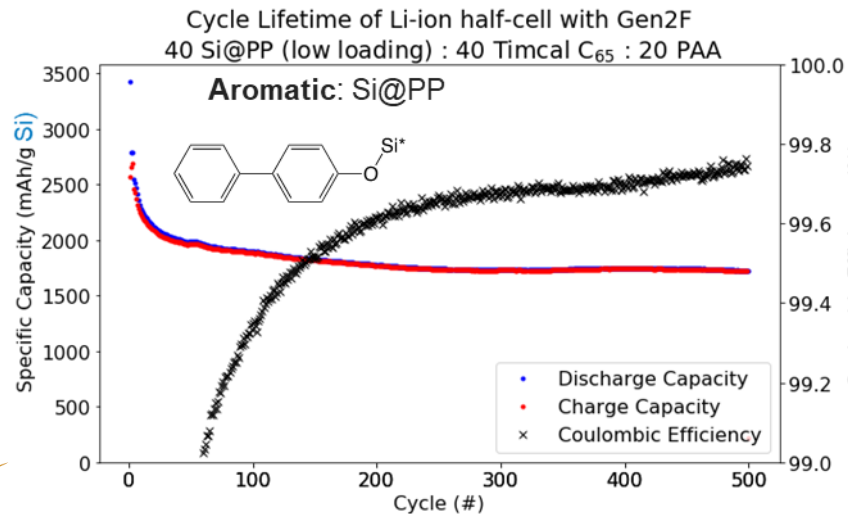
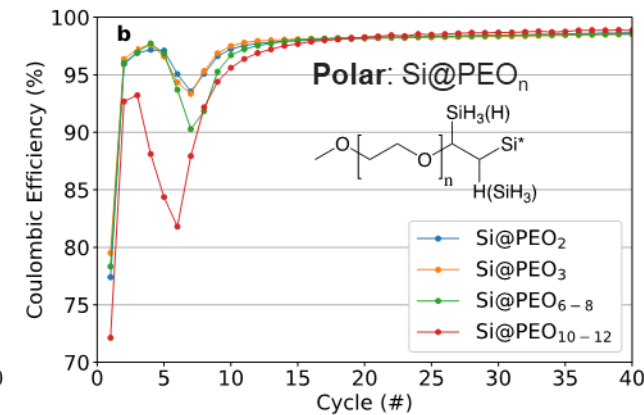
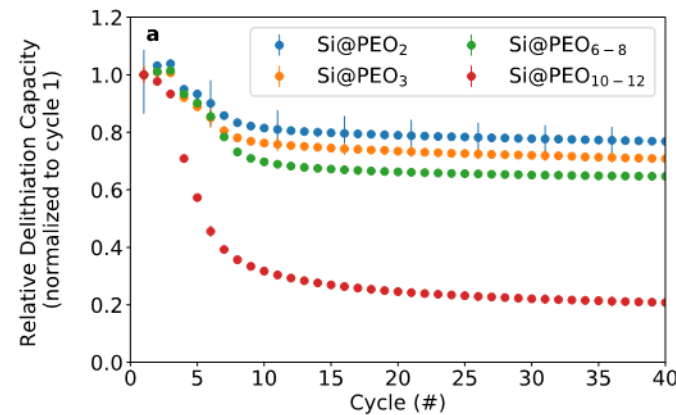
**Polar:** Si@PEO<sub>n</sub>



## Polar vs. non-polar:

- Non-polar groups block Li-ion conduction and electrochemically deactivate the Si
- Polar groups facilitate Li-ion conduction and improve capacity retention and CE

**Effect of polar ligand length:** Polar surfaces that are sufficiently long become electronically insulating and lower the reversible capacity of Si; long-term CE is largely independent of polar surface thickness

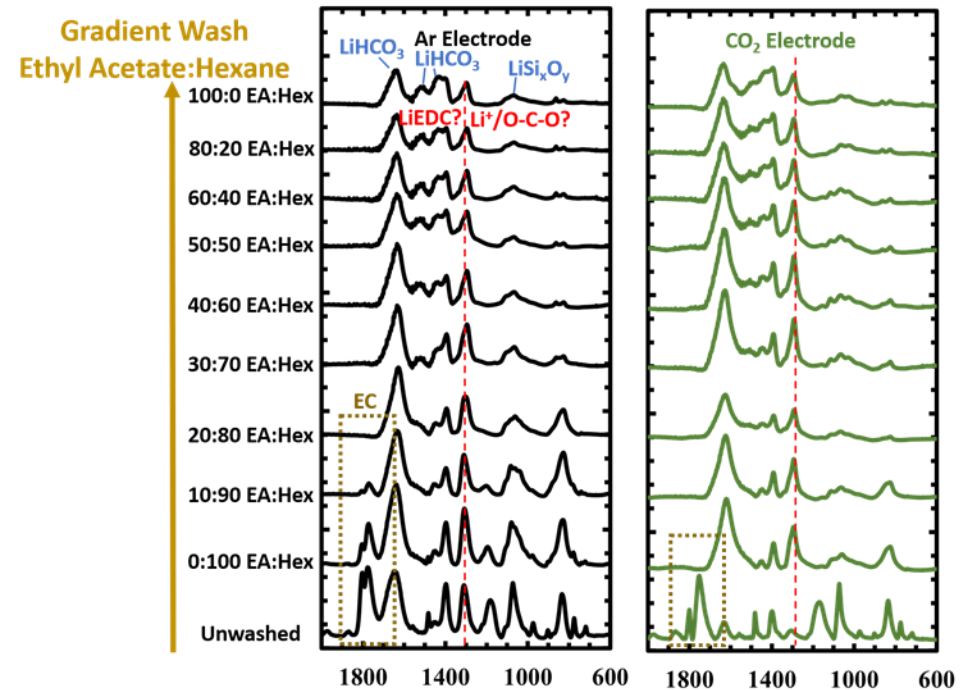


## Aromatic:

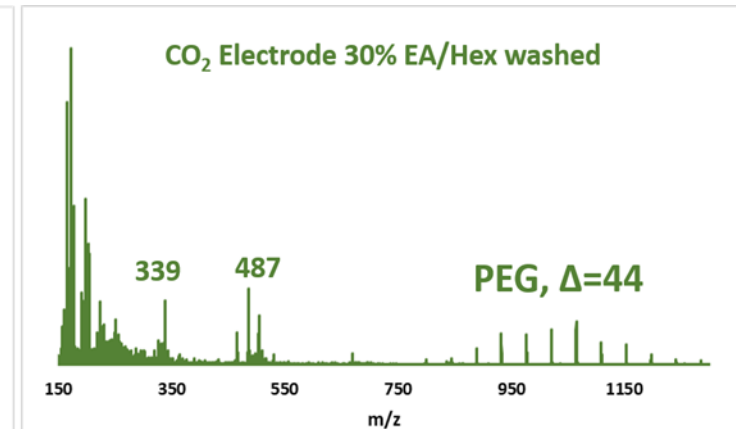
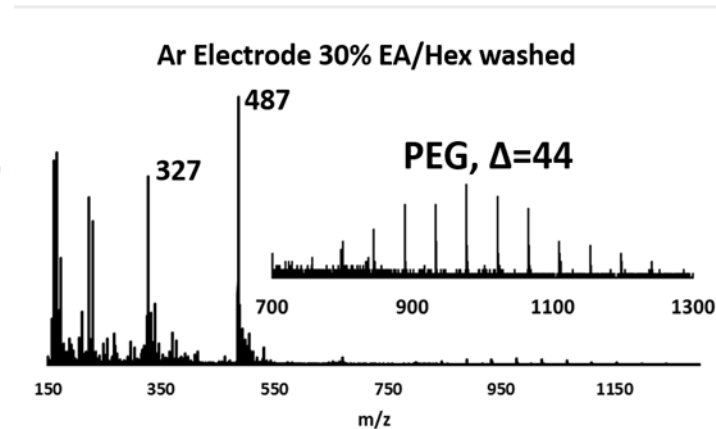
- Aromatic functionalized surfaces enable long cycle lifetimes due to good ionic and electronic conductivity
- Early cycle coulombic efficiency is still low (<99%) and results in significant amounts of irreversible Li consumption

# CO<sub>2</sub> has been reported to enhance silicon anode performance

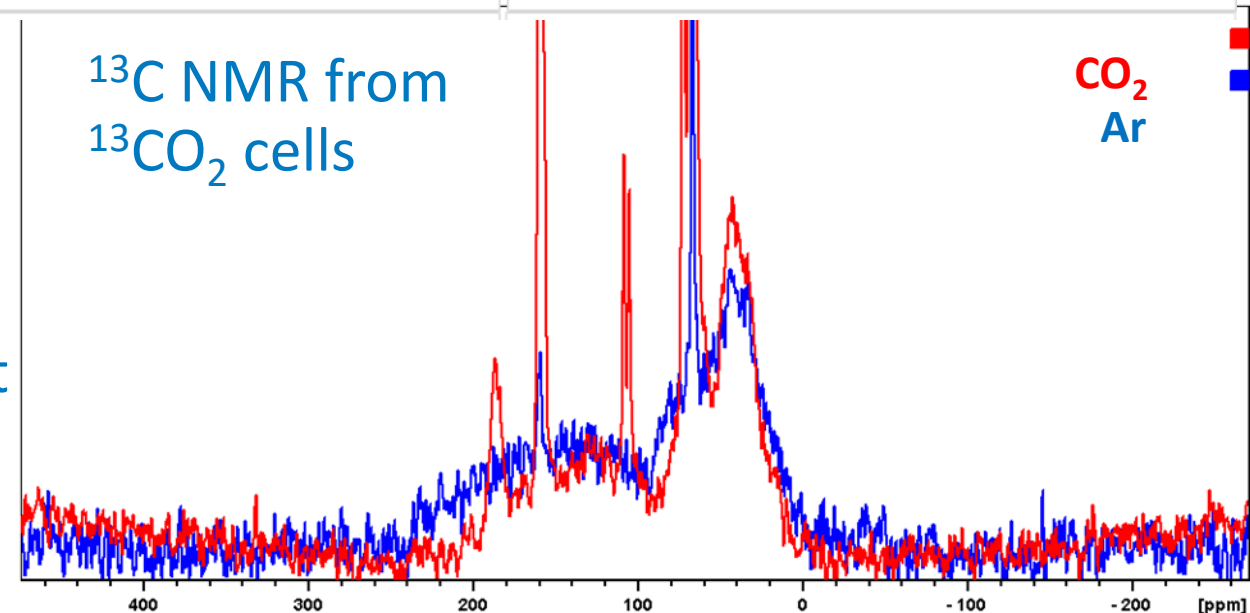
Result: Soluble SEI is significantly different with CO<sub>2</sub> resulting in more PEO like polymer species



TOF-MS Signal



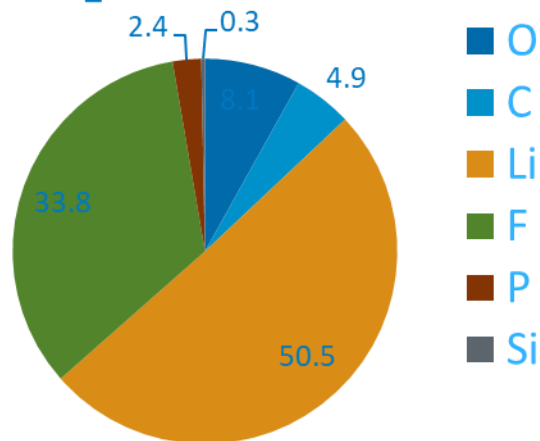
<sup>13</sup>C NMR from  
<sup>13</sup>CO<sub>2</sub> cells



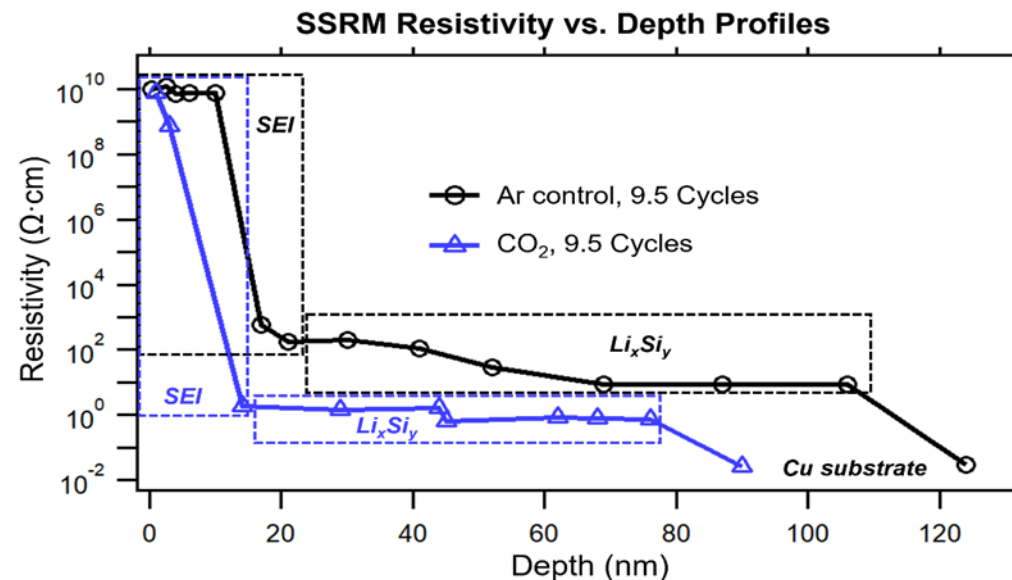
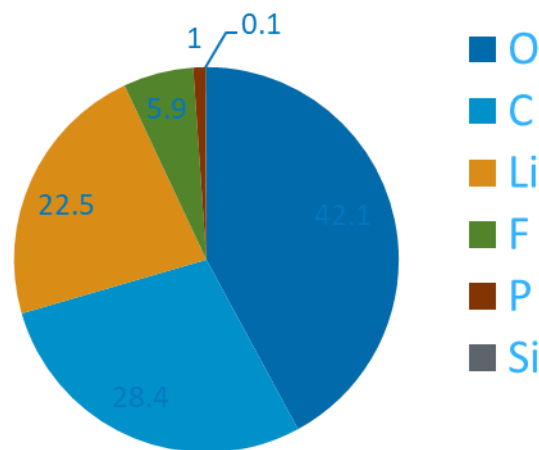
SEI with CO<sub>2</sub> has higher concentration of PEG like groups and different SEI species after cycling. But they are easy to remove in DMC. How do we fix?

# Result: CO<sub>2</sub> changes the Si SEI chemistry and thickness but not capacity retention

CO<sub>2</sub> XPS result



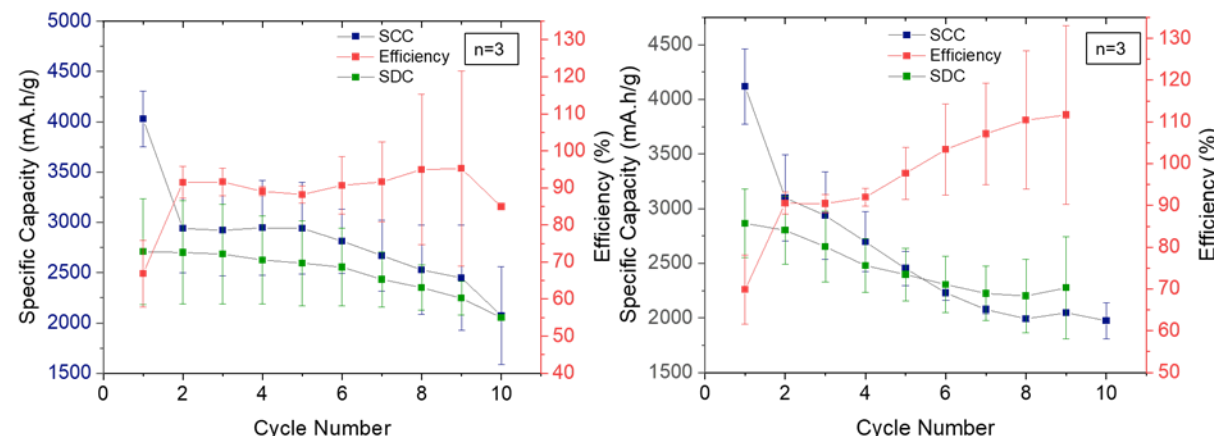
Ar XPS result



Post DMC wash we see insoluble part of the SEI is more inorganic (LiF like) with CO<sub>2</sub> and more organic without CO<sub>2</sub> – CO<sub>2</sub> appears to mimic FEC additive

DMC washed SEI is thinner

The changes that the presence of CO<sub>2</sub> induce in the SEI don't result in improved capacity retention



## Summary

- A team approach with rigorous sample and experimental control is at the heart of this project.
- The nature and life history of the silicon has a dramatic effect on the formation and evolution of the SEI on silicon.
- Alloys and the zintl phase show promise but the exact nature of the effect is still under investigation.
- Project is moving to a much more vertically integrated approach connecting fundamental results with cell builds.
- In our hands CO<sub>2</sub> does not improve performance.
- The nature of the silicon surface is a critical element in performance.
- Understanding of how changes affect the SEI chemistry is fundamental to progress.

# Proposed future work is subject to change based on funding levels.”

- Test protocols, (cyclic life and calendar life) will be employed for all silicon “advances” .
- Understanding the mechanical features of the SEI will be important.
- More focus on understanding the formation and evolution of the SEI in alloy systems.
- Identify solutions to SEI stability based upon SEISta understanding and direct synthesis of new silicon materials to take through to full cell efforts using a stage gate approach.

# CONTRIBUTORS AND ACKNOWLEDGMENT

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham, Steven Boyd, and David Howell

|                     |                        |                         |                   |                   |
|---------------------|------------------------|-------------------------|-------------------|-------------------|
| Adam Tornheim       | Daniel Abraham         | Jaclyn Coyle            | Matt Keyser       | Sisi Jiang        |
| Alexander Rogers    | David Hoelzer          | Jagjit Nanda            | Matthew Page      | Stephen Trask     |
| Alison Dunlop       | Dennis Dees            | Jason Zhang             | Maxwell Schulze   | Steve Harvey      |
| Andrew Colclasure   | Elisabetta Arca        | Jessica Dudoff          | Mike Carroll      | Sujoing Chae      |
| Andrew Jansen       | Eric Allcorn           | Jianlin Li              | Mingjian Wen      | Tingzheng Hou     |
| Andrew Norman       | Eric Sivonxay          | Zhengcheng Zhang        | Mowafak Al-Jassim | Trevor Martin     |
| Andriy Zakutayev    | Fernando Urias-Cordero | John Farrell            | Natalie Seitzman  | Vincenzo LaSalvia |
| Annalise Maughan    | Fulya Dogan            | John Moseley            | Nathan Neale      | Wade Braunecker   |
| Baris Key           | Gabriel Veith          | Johnson, Noah Mark      | Pauls Stradins    | Wei Tong          |
| Bertrand Tremolet   | Gao Liu                | Josefine McBrayer, D.   | Pengfei Cao       | Wenquan Lu        |
| Beth Armstrong      | Glenn Teeter           | Kandler Smith           | Polzin, Bryant J. | William Nemeth    |
| Brian Cunningham    | Greg Pach              | Kang Yao                | Ran Yi            | Xialolin Li       |
| Caleb Stetson       | Guang Yang             | Katharine Harrison      | Robert Kostecki   | Xiang Li          |
| Charlie Nguyen      | Haiyan Croft           | Katie Burdette-Trofimov | Robert tenent     | Yeyoung Ha        |
| Chelsea Cates       | Harvey Guthrey         | Kevin Zavadil           | Ryan Pekarek      | YoungHo Shin      |
| Chen Fang           | Hetal Patel            | Kristin Persson         | Sang Don Han      | Yunya Zhang       |
| Chen Liao           | Insun Yoon             | Lu Zhang                | Sang-Won Park     | Zhangxing Shi     |
| Christopher Apblett | Ira Bloom              | Marco Tulio Fonseca     | Sarah Frisco      | Zhenzhen Yang     |
| Christopher Johnson | Jack Deppe             | Rodrigues               | Sergiy Kalnaus    | Zhifei Li         |
| Chun Sheng Jiang    | Jack Vaughey           | Marisa Howe             | Shriram           | Zoey Huey         |
| Claus Daniel        |                        |                         | Santhanagopalan   |                   |

